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NMR Chemical Shifts. 2. Interpretation of the Carbon Chemical Shifts in Monocyclic Aromatic Compounds and Carbenes

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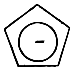
The physical basis of the well-known linear correlation between ^{13}C chemical shift and charge density in monocyclic aromatic ions has been investigated. Structures of the ions were calculated at the MP2/6-31G* level, and their chemical shifts were calculated using GIAO and IGAIM at the B3LYP/6-311+G(3df,2p) level using the MP2 geometries. The calculated tensor components of the shifts are in good accord with the experimental data. The linear correlation of chemical shift with charge was extended to CH_3^+ and planar CH_3^-, and the physics underlying this correlation has also been found to explain shielding trends for singlet carbenes. The tensor components along the in-plane axes for CH_3^- are close to the maximum diamagnetic shielding for carbon. The corresponding components for CH_3^+ are 700 ppm downfield from CH_3^-, largely resulting from paramagnetic current densities about the in-plane axes. On the other hand, the tensor components about the out-of-plane axis, resulting from magnetically induced current densities in the plane of these ions, are all essentially the same. The chemical shifts for these species are not directly related to the charge at carbon but instead depend on the difference in the occupancies of the p orbitals normal to the field direction. This is further supported by calculations of the shielding in C^{4+}, C^{2+}, and C^{4-}, all of which are more shielded than TMS.

1. Introduction

It has generally been assumed that there is a relationship between the charge density at a carbon and its NMR chemical shift.[1] In part, this is based on the linear relationship between the chemical shift and the symmetry determined charges in the series cyclopentadienyl anion (**1**), benzene (**2**), cycloheptatrienyl cation (**3**), and cyclooctatetraenyl dianion (**4**).[2] This correlation has been extended to the other monocyclic aromatic ions using both experimental data and IGLO calculations, and with the exception of cyclopropenyl cation, the original correlation was confirmed.[3] We were interested in further examining this relationship, and in doing so we have also made use of ab initio MO calculations of the chemical shifts. Our motivation has been to develop a physical basis for understanding these shifts in terms of concepts familiar to organic chemistry.[4]

The compounds to be examined in this report are **1**−**4** and the cyclononatetraenyl anion (**5**). The tensor components of the chemical shifts are of special interest since they provide additional information concerning the nature of the interactions that lead to the chemical shifts.



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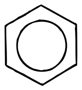

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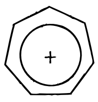

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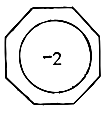

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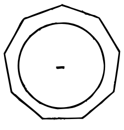

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It is now widely appreciated that ab initio calculations accurately mirror experimental results for first-row elements such as carbon.[5] As long as accuracies of a few ppm are sufficient, there are many methods which approach this computational problem with different strategies yielding comparable results. Good comparisons to shift anisotropies measured in solid-state NMR experiments have provided a great deal of confidence for calculating NMR shielding parameters. These advances in computational accuracy have unfortunately not been accompanied by concomitant strides in furthering our understanding of chemical shifts from a chemical perspective. The present study is an attempt to develop this type of understanding for the monocyclic aromatic ions from computer calculations. This series reported on here was chosen as the range of shifts spanned is a large fraction of the entire ^{13}C chemical shift scale and the dependence on charge is simple. In addition to calculating the shielding tensors for the molecules of interest, a number of calculations have also been performed for systems which are not readily accessible experimentally. Using this approach to extend the range of systems that can be studied in the laboratory has provided the additional insight needed to delineate the effects that give rise to the shielding trends observed in the experimentally tractable systems. The end result is that the ^{13}C shielding parameters of seemingly unrelated species such as singlet carbenes, methyl cation and anion, and charged planar aromatics can all be understood within a single simple model.

2. Calculated Chemical Shifts

It is known that the calculated chemical shifts are sensitive to the geometry used,[6] and therefore, for consistency, the structural data were obtained by MP2/6-31G* geometry optimizations (Table 1). As might be expected, the anions generally have longer C−C bonds than benzene or cycloheptatrienyl cation.

The shielding calculations were carried out using GIAO (gauge including atomic orbital)[7] and IGAIM (individual gauge atoms in molecules)[8] The latter obtains the nuclear shielding by integrating the shielding density derived from the current

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TABLE 1: MP2/6-31G* Calculated Structures and Energies[a]

compound	energy, H	r(CC), Å	r(CH), Å
cyclopentadienyl anion	−192.85530	1.4115	1.0899
benzene	−231.48719	1.3953	1.0871
cycloheptatrienyl cation	−269.79675	1.3985	1.0882
cyclooctatetraenyl dianion	−308.37665	1.4155	1.1025
cyclononatetraenyl anion	−347.15823	1.4029	1.0945
methyl cation	−39.32944		1.0887
methyl anion[b]	−39.58857		1.0840
isopropyl cation	−117.76065	1.4372	
tert-butyl cation	−156.95954	1.4592	
acetylene	−77.07622	1.2163	1.0659

[a] All electrons were included in the correlation correction. [b] Planar structure.

density for a molecule in a magnetic field, employing the specified nucleus as the origin for each of the sets of integrations. This method allows the calculation of the diamagnetic and paramagnetic shielding components on an MO basis.[9] The chemical shifts with respect to TMS are obtained using the calculated shielding of TMS, 183.1 ppm.

The chemical-shifts were calculated at the B3LYP/6-311+G(3df,2p) level that has been found to usually reproduce the experimental shifts in a satisfactory manner.[14] In this work, the shifts were calculated using both GIAO and IGAIM in Gaussian 94.[10] Since they employ quite different methods of solving the gauge problem, consistent results would suggest a satisfactory level of theory.

The chemical shifts of nuclei such as carbon result from both diamagnetic and paramagnetic terms.[11] The diamagnetic shielding leads to an upfield shift and is derived from just the ground-state charge distribution. The paramagnetic term that leads to the downfield shift results from the coupling of occupied and virtual orbitals by the perturbation of the applied magnetic field. From the form of the perturbing Hamiltonian it is easily shown that only those pairs of virtual and occupied orbitals that are connected by the z angular momentum operator (z being the magnetic field direction) can contribute to this term.

3. Methyl Cation and Anion

To gain more information on the diamagnetic and paramagnetic components of the chemical shift, we have calculated the shielding for methyl cation and planar methyl anion which represent a +1 and −1 charge, respectively, and would extend the chemical-shift scale with respect to compounds **1**−**5**. Although methyl anion is pyramidal, the planar structure was taken in order to have it correspond to the structures of the other compounds in this study. It was found that B3LYP/6-311+G** calculations gave differences in shielding between the two methods of up to 5 ppm, but the differences using the larger basis set were insignificant. Therefore, only the latter are reported in Table 3. The calculations yield the shielding of a carbon nucleus by the associated electrons. On this scale, tetramethylsilane (TMS) has a shielding of 183.1 ppm, which is in good agreement with the experimental value, 186.4 ppm.[12] The chemical shifts with respect to TMS are given in Table 3. The molecules are aligned so that the unique p orbital (p_z) lies along the z molecular axis. The similarity of the z axis components, despite the difference in charge, should be noted.

In the IGAIM procedure, the current density is first derived and the shielding density is calculated as the cross product of the current density and a vector from the carbon in question to the given point, divided by the distance cubed. The current density is interesting in itself and is shown for the two ions as contour plots in Figure 1. We have shown that in methyl cation, the full positive charge appears at the hydrogens[13] and with their depleted electron density, it is not surprising that the current density contours avoid the hydrogens. On the other hand, with methyl anion, most of the negative charge is found at the hydrogens and, consequently, the current density contours include the electron-rich hydrogens.

Integration of the current density may be carried out separately for each MO, giving the results shown in Table 2. Here, the MOs are labeled by the carbon atomic orbital that is involved. In common with all organic compounds, the 1s electrons give an upfield (diamagnetic) shielding of 200 ppm. Thus, the 1s electrons alone would make the chemical shift upfield from TMS. The 2s electrons give a smaller shielding of 20−25 ppm because of their greater distance from the nucleus (the effect goes as $1/r^3$ where r is the distance from the nucleus). These shielding values are essentially independent of charge. With methyl anion, the six p electrons contribute an additional 50 ppm shielding about the x and y axes, leading to a total shielding of 298 ppm or a chemical shift of −115 ppm with respect to TMS.

This appears to be close to the maximum diamagnetic shift for carbon. A carbon atom with all of its 2s and 2p filled (C^{4-}) has a calculated chemical shift of −103 ppm. Similarly, the chemical shift for the long axis of acetylene, which results exclusively from the diamagnetic circulation of the electrons, is −96 ppm.

With methyl cation, the shielding about the z axis is about the same as for methyl anion, despite the difference in charge. However, about the x and y axes, there are large paramagnetic deshielding terms derived from the coupling of the p_z orbital to either the p_x or p_y orbitals by the magnetic field. The net difference between methyl cation and methyl anion about these axes is over 700 ppm!

4. Benzene and the Aromatic Ions

The calculated tensor components (Table 3) are in good agreement with the available experimental data.[14] One would not expect perfect agreement because the calculations refer to nonvibrating molecules in the gas phase whereas the experimental data are for molecules having zero-point vibrations in the solid state.[15] In addition, the experimental data for the ions are for ion pairs in the solid state. The experimental tensor components have an uncertainty of about ±5 ppm. The agreement between experiment and theory gives us confidence that the calculated shifts for the methyl ions are meaningful.

The z component of the chemical-shift tensor has a small range, 10−35 ppm. This is typical of all simple alkenes (in ethylene it is 16 ppm calculated and 24 ppm observed). The larger chemical shift changes for benzene, and the cations are found along the x and y axes, here they are often deshielded with respect to a bare carbon nucleus.

A plot of the isotropic chemical-shifts for methyl cation and anion vs the charge is shown in Figure 2. Superimposed on the line formed from these two points are the isotropic chemical shifts for compounds **1**−**5**. It can be seen that the points for the latter compounds lie close to the line. One may also examine the tensor components of the shifts. In Figure 3, the x, y, and z components for methyl cation and anion are plotted against the charge. The larger in-plane (y) tensor components and the z components for **1**−**5** are superimposed on the line. The former again lie close to the line defined by the methyl ions, and the

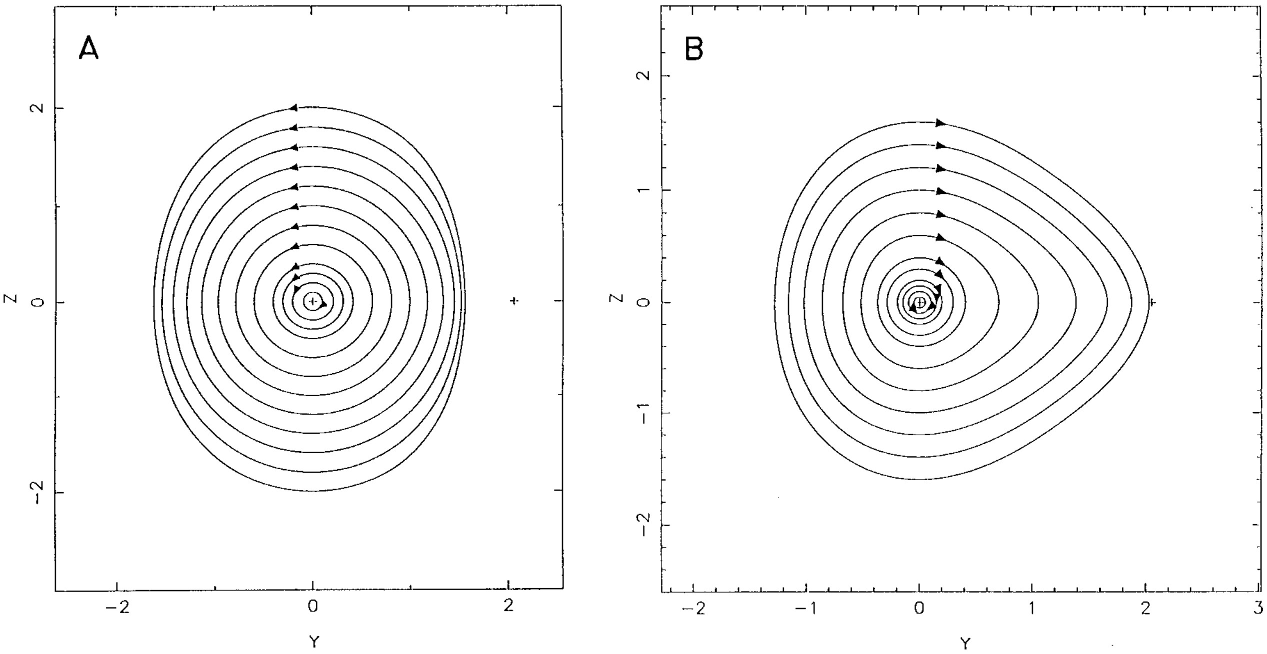
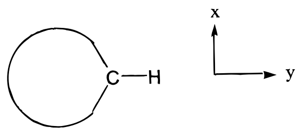


Figure 1. Current densities for methyl cation (A) and methyl anion (B). In each case, the field is applied normal to the plane of the plot and the molecule is aligned with the empty p orbital in the vertical direction, and a methyl hydrogen in the plane is indicated by a cross. With methyl anion, the current is clockwise everywhere, corresponding to shielding. With methyl cation, the current is counterclockwise (deshielding) everywhere except near the nucleus where it is clockwise (shielding from the 1s electrons).

TABLE 2: Shielding for CH_3^+ and CH_3^- on an MO by MO Basis

	MO					
component	1 1s	2 2s	3 2px	4 2py	5 2pz	total
			a. CH_3^+			
xx	200	28	13	−660		−419
yy	200	28	−660	13		−419
zz	200	18	−21	−21		176
isotropic	200	24	−223	−223		−221
			b. CH_3^-			
xx	200	19	11	−24	90	297
yy	200	19	−24	11	90	297
zz	200	16	−24	−24	12	180
iso	200	18	−12	−12	65	258

latter are essentially invariant with charge. Here, the tensor components are given for the molecular orientation shown below



5. Framework for Interpretation of Shielding Trends

To understand the change in shielding with the charge at a CH group in chemical terms, we wish to partition the total shielding into contributions from the different types of orbitals at carbon. This necessarily forces us to pick a particular gauge. A great deal of research has been devoted to addressing this issue from the standpoint of achieving accurate ab initio calculation of shielding constants.[16] While every choice of gauge has its advantages and adherents, from the chemist's perspective the simplest gauge choice is one centered on the nucleus in question. The partitioning of the shielding into paramagnetic and diamagnetic terms then largely parallels the classification of electrons into valence and core electrons, respectively, which in turn makes the connections between shielding trends and basic principles of chemistry somewhat more natural.

Using this choice of gauge origin, the diamagnetic currents affecting carbon shifts are dominated by the core s electrons as expected. The electrons in the p states also have diamagnetic currents from their first-order interaction with the applied magnetic field, but they produce small shielding fields at the nucleus. This can quantitatively be appreciated by considering the absolute shielding produced in the series C^{4+}, C^{2+}, and C^{4-}. The two carbon 1s electrons give a diamagnetic shielding of a carbon nucleus of about 200 ppm in all systems studied. This is found in the results of IGLO calculations[14] in which the shielding due to the 1s electrons for a variety of organic compounds is uniformly found to be 201 ppm and in GIAO and IGLO calculations of the shielding in C^{4+}, 202 ppm. The diamagnetic contribution from the two 2s electrons may be obtained from a calculation on C^{2+}, giving a much smaller additional 36 ppm upfield shift. In C^{4-} with six p electrons, the total shielding for carbon is 286 ppm (close to the long-axis tensor value for acetylene and diacetylene). This corresponds to a shift δ with respect to TMS of −103 ppm. Here, because of the symmetry of the p orbitals, there is no paramagnetic term. The total diamagnetic shielding attributable to the p electrons then is only 50 ppm out of 286 ppm. This trend is as expected, since the diamagnetic shielding field depends on the value of $1/r$ for the electrons involved. Thus, the diamagnetic shielding per electron for a 1s state is over 10 times as large as that for a 2p state.

The paramagnetic currents are of course of more interest to the chemist as they provide greater insight into the structure of the valence electrons. These are conveniently understood using the formula first derived by Ramsey[17] for the *zz* component of the shielding in the nucleus centered gauge:

$$\sigma_{zz}^{\,p} = -\frac{e^2\mu_o}{4\pi m_e^{\,2}}\sum_n \frac{\langle 0|l_z|n\rangle}{E_o - E_n}\left\langle n\left|\frac{l_z}{r^3}\right|0\right\rangle \qquad (1)$$

TABLE 3: Calculated Chemical Shifts Relative to TMS,[a] ppm, B3LYP/6-311+G(3df,2p)[b]

compound	component	GIAO	IGAIM	obs[c]
C^{4+}	all	−19	−19	
C^{2+}	all	−55	−55	
C^{4-}	all	−103	−103	
methane	all	−6	−7	
methyl cation	Isotropic	405	404	
	xx = *yy*	603	602	
	zz	10	7	
methyl anion[b]	Isotropic	−76	−75	
	xx = *yy*	−114	−114	
	zz	2	3	
cyclopentadienyl anion (**1**)	Isotropic	104	103	106
	xx	96	96	114
	yy	189	187	182
	zz	27	27	21
benzene (**2**)	Isotropic	135	134	130
	xx	145	144	146
	yy	248	247	234
	zz	11	10	9
cycloheptatrienyl cation (**3**)	Isotropic		161	167
	xx		187	168
	yy		278	280
	zz		19	22
cyclooctatetraenyl dianion (**4**)	Isotropic		100	
	xx		66	
	yy		200	
	zz		34	
cyclononatetraenyl anion (**5**)	Isotropic		114	
	xx		88	
	yy		226	
	zz		27	
isopropyl cation	Isotropic		332	
	xx		549	
	yy		437	
	zz		28	
tert-butyl cation	Isotropic		350	
	xx = *yy*		512	
	zz		28	
acetylene	Isotropic	73	73	70
	xx = *yy*	158	157	150
	zz	−96	−96	−90

[a] TMS shielding = 183.1 ppm. [b] The B3LYP/6-311+G(3df,2p)//MP2/6-31G* energies were C^{4+}, −32.38536; C^{2+}, −36.51295; C^{4-}, −25.83910; HC≡CH, −77.36120; $C_5H_5^-$, −193.59466; C_6H_6, −232.32756; $C_7H_7^+$, −270.75911; $C_8H_8^{-2}$, −307; $C_9H_9^-$, −348.43345. [c] The observed tensor components are taken from ref 14.

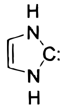
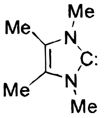
In this equation μ_o is the permeability of free space, e is the electron charge, m_e the electron mass, E_o and E_n the energies of the ground and nth electronic states, r the distance between the electron and the nucleus, and l_z the operator giving the angular momentum of the electron about the applied field, which is chosen to be along the z axis in the laboratory frame. This expression is summed over all electrons, in addition to being summed over the excited electronic states $|n>$ above the ground state $|0>$, in calculating the total paramagnetic shielding contribution.

The physical origin of paramagnetic shielding from the perspective of eq 1 is well understood. Under the influence of the applied magnetic field, the ground state $|0>$ is admixed with the unoccupied excited states $|n>$ depending on how they are connected by the angular momentum operator l_z. The smaller the energy difference $\Delta E = E_o - E_n$ and the closer the electrons are to the nucleus, the stronger the effect. Terms connecting fully occupied states are excluded from the sum simply because they occur twice with equal magnitude but opposite signs and thus are self-canceling.

While eq 1 is cast in terms of electronic states, it is also possible to recast it in terms of matrix elements involving atomic orbitals as discussed extensively by Pople in his early work on nuclear shielding.[18] This is permissible when one is trying to qualitatively understand very large shielding effects such as those under present consideration. The principal difference then is that the occupancies of individual atomic or hybrid orbitals must then be taken into account. As will shortly become apparent, this is actually the principal attraction for using such a framework to describe shielding for sp^2-hybridized carbon centers.

For a qualitative model we will adopt a single sp^2-hybridized carbon center in an organic molecule. Following Slichter,[19] we can consider the bonding of this fragment to the rest of the molecule as being described by a crystal field. This crystal field determines the energies of the molecular orbitals that the sp^2

TABLE 4: GIAO Calculated Chemical Shifts for Carbene Carbons, 6-311++G(3df,2p)[a]

compound	component	HF	B3LYP	MCSCF[b]
CH_2	iso	1592	1335	901
	xx	4313	3492	2303
	yy	482	541	420
	zz	−19	−27	−27
$C(NH_3^+)_2$	iso	779	728	
	xx	2007	1804	
	yy	243	288	
	zz	86	93	
CF_2	iso	326	315	284
	xx	689	621	580
	yy	143	166	141
	zz	147	158	131
$C(NH_2)_2$	iso	281	256	
	xx	588	511	
	yy	224	227	
	zz	31	29	
	iso	249	227	209
	xx	513	452	431
	yy	196	193	172
	zz	39	38	23
	iso	251	229	
	xx	466	401	
	yy	201	195	
	zz	85	91	

[a] The orientation is the same as for the compounds in Table 2, with the y axis along the C-lone pair and the z axis being out-of-plane. The MP2/6-311+G** geometries were used with the smaller compounds, and MP2/6-31G* geometries were used for the two cyclic carbenes. [b] Reference 23.

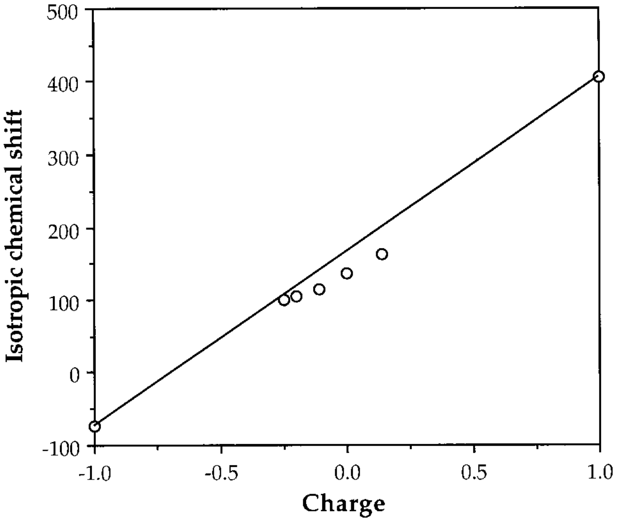


Figure 2. Correlation between the isotropic chemical shifts and the charge. The circles correspond to (left to right) CH_3^-, $C_8H_8^{-2}$, $C_5H_5^-$, $C_9H_9^-$, C_6H_6, $C_7H_7^+$, and CH_3^+.

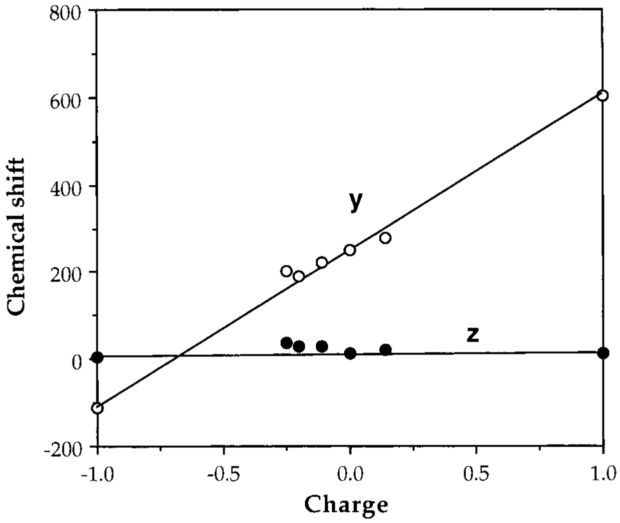


Figure 3. Correlation between the tensor components of the chemical shifts and the charge. The open circles correspond to the *yy* components, and the closed circles give the *zz* (out-of-plane) components. The compounds are the same as in Figure 2.

carbon center participates in. Changes in the crystal field, i.e., in the substituents, will primarily affect the energy denominator. If we now consider the matrix elements of l_z it is easy to understand the large anisotropy of the shielding seen by the carbon in these centers.

Placing the applied field along the molecular z axis, the orbitals with p_x character are connected by the l_z operator to those with p_y character and vice versa. Since the energies of the lowest-lying virtual orbitals with such character are quite high, the paramagnetic shielding will be small in this direction. If the applied field is, however, placed along the molecular x axis, the situation is quite different. The l_z operator now mixes the p_z orbital with those having p_y character. Excited states involving the p_z atomic orbital of the sp^2 fragment are much lower in energy and, therefore, give rise to larger paramagnetic shielding. In the atomic orbital description one also sees that the p_z occupancy is important. When the p_z orbital is completely empty it is a virtual orbital, and this mixing term will dominate the paramagnetic shielding. On the other hand if it is completely filled, the paramagnetic contribution will go to zero for the reasons discussed earlier. For fractional occupancies, the shielding that occurs will be the appropriate linear combination of these two extremes.

6. Model for ^{13}C Shielding in sp^2 Centers

For the planar monocyclic aromatic ions, the qualitative model just described is quite applicable, as the carbon centers are essentially sp^2 sites with variable occupancy in the p_z orbital. Shielding with the field along the p_z orbital is not expected to vary among these systems as the orbitals mixed by the perturbation do not involve the π system. This is in fact what is observed both experimentally and in computations.

The shielding observed when the field is placed perpendicular to the p_z orbital leads to a large paramagnetic current from the mixing of this orbital with the in-plane sp^2 orbitals. The energy separation of these orbitals is not expected to vary greatly among the systems investigated. In addition, the centers remain largely sp^2 hybridized, thus we would also not expect the orbital angular momentum matrix elements to vary much either. The remaining variable is the occupancy of the p_z orbital, which is reflected in the changes in fractional charge density at the carbons studied.

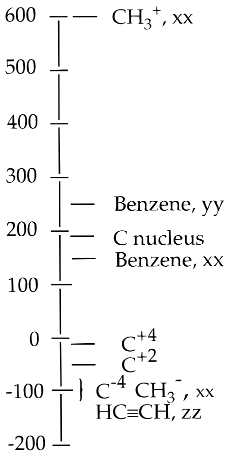


Figure 4. Range of ^{13}C chemical shifts relative to TMS as zero. The carbenes are for the most part off-scale at the top of the plot.

At one extreme we have the CH_3^- in which the p_z orbital is filled. In accord with the simple model presented, no net paramagnetic shielding arises from mixing with this orbital as equal and opposite currents would arise from the second-order shielding term in the Ramsey formula. The calculations support this, the shielding observed perpendicular to the p_z orbital is no different than found in C^{4-} or along the long axis of acetylene. The fact that this shift is so invariant to charge emphatically illustrates that charge in itself can only indirectly affect nuclear shielding.

By removing the two electrons from the p_z orbital we should then maximize the paramagnetic term. This leads us to the shielding for CH_3^+, which is the most paramagnetically shifted species of the ones described above. This single term involving the p_z orbital changes by 700 ppm in removing these two $2p_z$ electrons. Here, the carbon is strongly deshielded, even with respect to a bare carbon atom because of the large paramagnetic term. The range of chemical-shifts relative to tetramethylsilane is illustrated in Figure 4.

With these two shifts in hand it is a simple matter to explain the shielding pattern observed for the monocyclic aromatic compounds. For these species the p_z orbital is partially occupied, implying that they are described by a state which is a linear combination of those describing the methyl anion and cation. Therefore, their in-plane shifts should lie on a line connecting these two extremes, with the position determined by the partial occupancy of the $2p_z$ orbital. As Figure 3 illustrates, this is largely the case.

With the realization that it is orbital occupancy rather than charge that is the determining factor in these shifts, it is of some interest to further consider systems which may be related. It was of interest to see if substitution would markedly change the chemical shift of the methyl cation. Calculations on isopropyl cation and *tert*-butyl cation (Table 2) show that the in-plane components are not changed much and that the component along the empty p orbital has about the same value as for the other ions.[20]

7. Comparison with Carbenes

Singlet methylene may formally be considered to be formed by the removal of a proton from methyl cation. Thus, it retains an empty p orbital and instead of one C−H bond of the cation it has a lone pair. Calculations for methylene have found remarkable deshielding for the tensor component that is in the plane of the molecule and is normal to the lone pair.[21] To examine the effects of electron correlation, the GIAO chemical shifts have been calculated at the HF/6-311+G(3df,2p) level as well as using the B3LYP[22] functional and are given in Table 3.

The large deshielding for the *xx* component of methylene is reproduced by these calculations. Whereas the previous DFT calculations found an increase in the deshielding with respect to HF, the present calculations lead to shielding with respect to the HF calculation. This is in agreement with the results of a recent multiconfiguration IGLO calculation that gave a shift of 2300 ppm.[23] Our DFT-level calculations are about halfway between the HF and MCSCF values. Among the carbenes studied herein, one might expect that methylene would benefit most from a multiconfiguration treatment. With difluorocarbene and imidazoyl-2-ylidine, the agreement between the present DFT shifts and the MCSCF values is quite good.

The large paramagnetic deshielding as compared to methyl cation is due to the nonbonded character of the electrons in the lone pair which leads to a larger paramagnetic current density. It should be possible to reduce this term by introducing substituents that would either donate charge density to the empty p orbital or decrease the p character of the lone pair. A strong electron-withdrawing substituent would, in accord with Bent's rule,[24] demand high p character from the carbon to which it is bonded, and in the present case this would result in a loss of p character for the lone pair electrons. An NH_3^+ group would have this characteristic and does not have a lone pair that could donate electron density to the empty p orbital. The calculated chemical-shift components for $C(NH_3^+)_2$ are given in Table 3. In accord with expectation, the strong deshielding for the *xx* component found with CH_2 is markedly reduced.

When the substituent is both electron withdrawing and a potential π-donor, as with F and NH_2, one might expect both the reduction in p character for the lone pair electrons and donation of π-electron density into the empty p orbital of the carbene center. Previous calculations[21] have shown that the *xx* deshielding is further reduced in CF_2 and $C(NH_2)_2$, and this is confirmed by the present calculations (Table 4).

There is one carbene for which experimental data are available, 1,3,4,5-tetramethylimidazoyl-2-ylidine.[21] The chemical shifts calculated at the above theoretical levels are given in Table 4 along with the shifts for the compound having no methyl groups. The experimental tensor components of the chemical shift are $xx = 370 \pm 20$, $yy = 177 \pm 18$, and $zz = 82 \pm 15$ ppm, which may be compared with the calculated values $xx = 401$, $yy = 195$, and $zz = 91$. The agreement is satisfactory.

Conclusions

The chemical shifts of the aromatic ions are mainly produced by a paramagnetic term whose magnitude decreases linearly with the occupancy of the out-of-plane p orbital. It has a value of about zero for an occupancy of 2 and changes linearly by about −700 ppm on going to an occupancy of 0. Despite this large change, the tensor component about the axis of the p orbital hardly changes. Thus, there is not a correlation with the overall charge at the carbon but rather only with the charge in the out-of-plane p orbital.

In a classical picture, the paramagnetic shift is facilitated by having an empty p orbital into which an electron can "jump" in the presence of a magnetic field. As the occupancy of this orbital is increased, the jump is retarded, and when it is doubly occupied (CH_3^-), the jump is no longer possible and there is little if any paramagnetic current density. The diamagnetic shielding in this case is over 300 ppm relative to a carbon nucleus, leading to a chemical shift with respect to TMS of −108 ppm. The paramagnetic component for CH_3^+ is on the order of 700 ppm.

A further increase in the magnitude of the paramagnetic shift is found with the singlet carbenes in which the p component of the lone-pair electrons is less strongly bound than in the cations, leading to an increase in the paramagnetic deshielding. The latter may be reduced either by decreasing the p character of the lone pair electrons or by donating π-electron density into the empty p orbital at the carbene center.

The combination of experimental data, computer simulations of that data, and computer experiments on experimentally inaccessible systems provides a very useful framework for developing insight into the origins of chemical shifts. In this example, the approach has made it possible for us to identify the primary factors leading to a ^{13}C shielding trend in terms of chemically familiar factors, i.e., orbital occupancy. We expect this approach to be useful in understanding the fundamentals of ^{13}C shielding in many more systems and for couching their discussion in terms of familiar concepts of bonding, hybridization, and polarizability.

Calculations

The ab initio calculations were carried out using Gaussian 94.[20] The integration of the shielding densities from the IGAIM calculations were carried out using a modified version of PROAIM.[31]

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